

09/21/99

Jc674 U.S. PRO

**UTILITY PATENT APPLICATION TRANSMITTAL
(Large Entity)***(Only for new nonprovisional applications under 37 CFR 1.53(b))*Docket No.
96B037/3Total Pages in this Submission
35**TO THE ASSISTANT COMMISSIONER FOR PATENTS**Box Patent Application
Washington, D.C. 20231

Transmitted herewith for filing under 35 U.S.C. 111(a) and 37 C.F.R. 1.53(b) is a new utility patent application for an invention entitled:

Olefin Polymerization Process With Alkyl-Substituted Metallocenes

and invented by:

Joseph C. Floyd, et al.Jc678 U.S. PRO
09/400568
09/21/99If a **CONTINUATION APPLICATION**, check appropriate box and supply the requisite information:☐ Continuation ☒ Divisional ☐ Continuation-in-part (CIP) of prior application No.: 08/899,902

Which is a:

☐ Continuation ☐ Divisional ☐ Continuation-in-part (CIP) of prior application No.:

Which is a:

☐ Continuation ☐ Divisional ☐ Continuation-in-part (CIP) of prior application No.:

Enclosed are:

Application Elements

1. ☒ Filing fee as calculated and transmitted as described below
2. ☒ Specification having 28 pages and including the following:
 - a. ☒ Descriptive Title of the Invention
 - b. ☒ Cross References to Related Applications *(if applicable)*
 - c. ☐ Statement Regarding Federally-sponsored Research/Development *(if applicable)*
 - d. ☐ Reference to Microfiche Appendix *(if applicable)*
 - e. ☒ Background of the Invention
 - f. ☒ Brief Summary of the Invention
 - g. ☒ Brief Description of the Drawings *(if drawings filed)*
 - h. ☒ Detailed Description
 - i. ☒ Claim(s) as Classified Below
 - j. ☒ Abstract of the Disclosure

UTILITY PATENT APPLICATION TRANSMITTAL
(Large Entity)

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35

Application Elements (Continued)

3. ☒ Drawing(s) *(when necessary as prescribed by 35 USC 113)*

- a. ☒ Formal Number of Sheets 2
- b. ☐ Informal Number of Sheets _____

4. ☐ Oath or Declaration

- a. ☐ Newly executed *(original or copy)* ☐ Unexecuted
- b. ☒ Copy from a prior application (37 CFR 1.63(d)) *(for continuation/divisional application only)*
- c. ☐ With Power of Attorney ☐ Without Power of Attorney
- d. ☐ DELETION OF INVENTOR(S)
Signed statement attached deleting inventor(s) named in the prior application,
see 37 C.F.R. 1.63(d)(2) and 1.33(b).

5. ☒ Incorporation By Reference *(usable if Box 4b is checked)*

The entire disclosure of the prior application, from which a copy of the oath or declaration is supplied under Box 4b, is considered as being part of the disclosure of the accompanying application and is hereby incorporated by reference therein.

6. ☐ Computer Program in Microfiche *(Appendix)*

7. ☐ Nucleotide and/or Amino Acid Sequence Submission *(if applicable, all must be included)*

- a. ☐ Paper Copy
- b. ☐ Computer Readable Copy *(identical to computer copy)*
- c. ☐ Statement Verifying Identical Paper and Computer Readable Copy

Accompanying Application Parts

8. ☐ Assignment Papers *(cover sheet & document(s))*

9. ☐ 37 CFR 3.73(B) Statement *(when there is an assignee)*

10. ☐ English Translation Document *(if applicable)*

11. ☐ Information Disclosure Statement/PTO-1449 ☐ Copies of IDS Citations

12. ☒ Preliminary Amendment

13. ☒ Acknowledgment postcard

14. ☒ Certificate of Mailing

☐ First Class ☒ Express Mail *(Specify Label No.):* EL327144474US

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35

Accompanying Application Parts (Continued)

15. ☐ Certified Copy of Priority Document(s) *(if foreign priority is claimed)*

16. ☒ Additional Enclosures *(please identify below):*

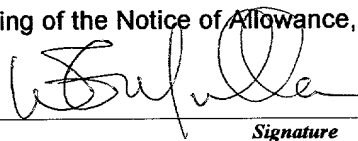
Associate Power of Attorney

Fee Calculation and Transmittal

CLAIMS AS FILED

For	#Filed	#Allowed	#Extra	Rate	Fee
Total Claims	10	- 20 =	0	x \$18.00	\$0.00
Indep. Claims	1	- 3 =	0	x \$78.00	\$0.00
Multiple Dependent Claims (check if applicable) <input type="checkbox"/>					\$0.00
BASIC FEE					\$760.00
OTHER FEE (specify purpose)					\$0.00
TOTAL FILING FEE					\$760.00

- ☐ A check in the amount of _____ to cover the filing fee is enclosed.
- ☒ The Commissioner is hereby authorized to charge and credit Deposit Account No. _____ as described below. A duplicate copy of this sheet is enclosed.
- ☒ Charge the amount of \$760.00 as filing fee.
 - ☒ Credit any overpayment.
 - ☒ Charge any additional filing fees required under 37 C.F.R. 1.16 and 1.17.
 - ☐ Charge the issue fee set in 37 C.F.R. 1.18 at the mailing of the Notice of Allowance, pursuant to 37 C.F.R. 1.311(b).


Signature

William G. Muller
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(281) 834-2671

Dated: September 21, 1999

cc: MLHarris

"PATENT"

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

<i>In re</i> APPLICATION of:	§	BEFORE THE EXAMINER
Joseph C. Floyd, et al	§	Unassigned
SERIAL NO.: Divisional Application of	§	Group Art Unit: Unassigned
08/899,902	§	
FILED: September 21, 1999	§	Attorney Docket No. 96B037/3
FOR: Olefin Polymerization Process With	§	Baytown, Texas
Alkyl-substituted Metallocenes	§	September 21, 1999

Commissioner of Patents and Trademarks
Washington, D.C. 20231

PRELIMINARY AMENDMENT UNDER 37CFR 1.115

Dear Sir:

This divisional is being filed from parent application 08/899,902, filed July 16, 1997, for claims 9-18, those claims having been identified as non-elected in the parent application. Before calculation of fees due it is requested that the following amendments be entered in this application.

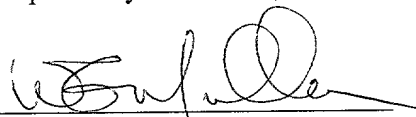
IN THE CLAIMS

Please cancel claims 1-8.

CONCLUSION

Claims 9-18 are now pending and all claims fees should be based on those alone.

Respectfully submitted,


William G. Muller
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**Olefin Polymerization Process
With Alkyl-substituted Metallocenes**

5 Related applications

This application is based upon the U.S. provisional application Ser. No. 60/021841 filed July 16, 1996.

Field of the Invention

10 The invention relates to a polymerization process for olefinically unsaturated monomers utilizing alkyl-substituent containing metallocenes to achieve polymer products having narrow composition distributions, low melt index ratios, and, optionally, high melt strength.

15 Background of the Invention

20 The use of metallocene compounds in catalyst systems for the polymerization of olefinically unsaturated olefins is well known in the art. Metallocene compounds have been defined as organometallic coordination compounds obtained as a cyclopentadienyl derivative of a transition metal or metal halide. Three types are representative: biscyclopentadienyl Group 4 metal compounds, biscyclopentadienyl Group 5-10 metal compounds and monocyclopentadienyl Group 4 and 5 metal compounds. In these categories are included those having alkyl-substituents on one or both cyclopentadienyl rings, both bridged metallocenes and unbridged metallocenes where the bridging if present is between one cyclopentadienyl ring ligand and another, or one cyclopentadienyl ring ligand and a heteroatom ligand of the transition metal. Syntheses of these compounds are well known and typically comprise the reaction of one or more selected cyclopentadienide compound with a transition metal halide.

30 Metallocenes generally are capable of narrow molecular weight distributions (MWD) in view of their typically yielding single-site catalysts when activated. However, capabilities as to compositional distributions (CD) and melt index ratios (MIR) vary widely,

particularly when the transition metal compounds are immobilized on particulate supports so as to form heterogeneous catalyst systems. Polymer products used in certain applications benefit from low MIR. The optical properties are improved when polymer fractions, typically comprised in the polymerization reaction product of any coordination polymerization catalysts, are as similar as possible. Additionally, narrow CD polymers typically have good optical properties, low levels of extractables and low blocking attributes. The narrow CD also is indicative of narrow melting point distribution which is of particular importance for film manufacturers.

10 Unbridged biscyclopentadienyl metallocene compounds having alkyl substituents said to be suitable for olefin polymerization, particularly heterogeneous polymerization process conditions, are described in U.S. patent 5,470,811. The catalysts comprise preferably at least two alkyl substituents on each and provide broad molecular weight distribution, high molecular weight and narrow composition distributions. Table II
15 examples 11-13 illustrate the use of $(1,3\text{-Me-n-BuCp})_2\text{ZrCl}_2$, $(1,2\text{-Me-n-BuCp})_2\text{ZrCl}_2$ and $(\text{n-Pr-Cp})_2\text{ZrCl}_2$ for copolymers having I_{21}/I_2 (defined as melt index ratio, MIR, measured in accordance with ASTM D-1238) values from 17.9 to 23.2 and MWD (M_w/M_n) values of from 2.5 to 3.7. Utility of the copolymers in film products and background for film preparation are disclosed. See also, WO 96/00246 for a description of multiply substituted
20 cyclopentadienyl ring-containing metallocenes and their use in gas phase polymerization processes where low melt indices or high molecular weights are sought.

 Bridged biscyclopentadienyl metallocenes useful for gas phase polymerization are disclosed in European Patent Application 0 659 773 A1. The cyclopentadienyl moieties
25 may be substituted with one or more substituents R, the catalysts are said to be suitable for the production of long chain branch-containing polyethylene when used in the process described. Values for I_{21}/I_2 of 56 to 110 are illustrative of the invention, the comparative examples illustrate values of 37 to 47.

Summary of the Invention

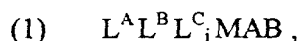
The invention comprises an olefin polymerization process comprising contacting ethylene alone or with one or more olefinically unsaturated comonomers with a Group 3-6
5 metallocene catalyst compound comprising one π -bonded ring having one or more C_3 or greater hydrocarbyl, hydrocarbylsilyl or hydrocarbylgermyl substituent, said substituent bonded to the ring through a primary carbon atom; and, 2) where a metallocene containing two π -bonded rings, the total number of substituents on the rings is equal to a number from 3 to 10, said rings being asymmetrically substituted where the number of substituents is 3
10 or 4. In a preferred embodiment compound containing two π -bonded rings, the rings are covalently bridged and a C_3 or greater hydrocarbyl, hydrocarbylsilyl or hydrocarbylgermyl substituent is at its ring 3 or 4 position with respect to the bridge. Where the metallocene contains only one π -bonded ring, it will preferably be bridged to a Group 15 or 16
15 heteroatom, said heteroatom preferably containing a 2° or 3° Group 14 atom containing hydrocarbyl, hydrocarbylsilyl or hydrocarbylgermyl substituent group of 1 to 20 non-hydrogen atoms. The term substituent when referring to those groups substituted on the rings includes essentially hydrocarbyl, hydrocarbylsilyl or hydrocarbylgermyl groups having from about 1 to 30 Group 14 atoms. Two adjacent ring substituent groups may be joined
20 so as to form a fused ring system, for example, unsubstituted or further substituted indenyl, fluorenyl or azulenyly groups. The invention process is particularly suitable for preparing ethylene copolymers having an MIR less than about 35, preferably less than about 30, and for certain embodiments less than about 20, and narrow CD, such as those having a comonomer distribution breadth index (CDBI) equal to or above 60, even at high comonomer incorporation rates. Ethylene copolymers having improved melt strength while
25 retaining the low MIR and narrow CD are also enabled by use of invention metallocene compounds containing two π -bonded rings covalently bridged to each other, with the C_3 or greater hydrocarbyl, hydrocarbylsilyl or hydrocarbylgermyl substituent being bonded at the 3 or 4 position on one of the rings, where the ring carbon covalently bonded to the bridge is counted as the 1 position.

Brief Description of the Figures

FIG. 1 is a Differential Scanning Calorimetry (DSC) measurement of polymer made according to the invention in Example I. FIG. 2 is a comparative DSC measurement of polymer made with a catalyst of the prior art. A comparison of the figures illustrates the narrow melting point distribution achieved using the invention catalyst exemplified.

Detailed Description of the Invention

The preferred Group 4 catalyst compounds comprising one π -bonded ring can be represented by the formula :



where $L^A L^B L^C_i MAB$ is the invention transition metal metallocene compound. More specifically, L^A is a substituted cyclopentadienyl or heterocyclopentadienyl ancillary ligand π -bonded to M; L^B can be a member of the class of ancillary ligands defined for L^A , or can be J, a heteroatom ancillary ligand σ -bonded to M; the L^A and L^B ligands may be covalently bridged together through a Group 14 element linking group, preferably the Group 14 element being carbon or silica; L^C_i is an optional neutral, non-oxidizing ligand having a dative bond to M (typically i equals 0 to 3); M is a Group 4 transition metal; and, A and B are independently monoanionic labile ligands, each having a σ -bond to M which can be broken for abstraction purposes, optionally bridged to each other or L^A or L^B , by a suitable activator and into which a polymerizable monomer or macromonomer can insert for coordination polymerization, or are ligands which can be converted to such; wherein at least one of L^A or L^B has at least one C_3 or greater hydrocarbyl, hydrocarbylsilyl or hydrocarbylgermyl substituent bonded to the ring through a primary carbon atom.

Either of L^A or L^B may be a cyclopentadienyl-group containing ring which is substituted with from two to five substituent groups R. When both are cyclopentadienyl-group containing rings, L^A or L^B may be a cyclopentadienyl ring with one substituent and the other a substituted cyclopentadienyl ring with two or more substituents. Each

substituent group R is, independently, a radical selected from hydrocarbyl, hydrocarbylsilyl or hydrocarbylgermyl having from 1 to 20 carbon, silicon or germanium atoms, substituted hydrocarbyl, hydrocarbylsilyl or hydrocarbylgermyl radicals as defined wherein one or more hydrogen atoms is replaced by a halogen radical, an amido radical, a phosphido radical, an alkoxy radical, an aryloxy radical or any other radical containing a Lewis acidic or basic functionality; C₁ to C₂₀ hydrocarbyl-substituted metalloid radicals wherein the metalloid is selected from the Group IV A of the Periodic Table of Elements; halogen radicals; amido radicals; phosphido radicals; alkoxy radicals; or alkylborido radicals; or, may be a cyclopentadienyl ring in which at least two adjacent R-groups are joined together and along with the carbon atoms to which they are attached form a C₄ to C₂₀ ring system which may be saturated, partially unsaturated or aromatic, and substituted or unsubstituted, the substitution being of one or more R groups as defined above.

Either or both of L^A or L^B may similarly be a heterocyclopentadienyl ancillary ligand π -bonded to M. The term "heterocyclopentadienyl" means here a 5-member ring analogous to a cyclopentadiene ring wherein at least one carbon atom at any position in the ring has been replaced with a non-carbon Group 14 or 15 element. Preferably the non-carbon elements are selected from the group consisting of germanium, silicon, nitrogen or phosphorous. The Group 14 or Group 15 heterocyclopentadienyl moieties are analogous to a cyclopentadienyl moiety which possesses a formal charge -1, making it formally a monoanionic ligand. And, though cyclopentadienyl rings are typically described as being "*eta*-5" bonded to the transition metal in metallocenes, other forms of π -bonding, *eta*-3 through *eta*-4, may additionally be possible with the Group 14 or 15 heterocyclopentadienyl ligands of the invention and thus are included within the scope of the invention. Such heterocyclopentadienyl ligands are addressed in U.S. patent 5,434,116, International publication WO 95/04087, Japanese application 08-24751 and co-pending application U.S. serial no. 60/041258 filed 3/17/97, each is incorporated by reference for purposes of U.S. patent practice.

The C₃ or greater hydrocarbyl, hydrocarbylsilyl or hydrocarbylgermyl substituent bonded to either the L^A or L^B ring through a primary carbon atom is preferably an n-alkyl substituent, such as, n-propyl, n-butyl, n-pentyl, n-dodecyl, etc. Substituents having a

primary carbon attached to the ring may be branched after that carbon, examples include 2-ethylbutyl, 2-methylpropyl, 2-cyclohexylethyl, and benzyl. The primary carbon-containing substituent is attached to either of the L^A or L^B rings and is preferably the only substituent on the ring to which it is attached, or is the substituent with the greatest number of non-hydrogen atoms. Additionally, for invention compounds containing a Group 14 atom-containing bridging group between the L^A and L^B rings, the C_3 or greater, primary carbon-containing substituent of the invention is preferably located at the 3 or 4 position, counting from the atom in the ring covalently bonded to the bridge, preferably the 3 position.

J as referred to above is a Group 15 or 16 heteroatom which may be substituted with one R' group when J is a group 15 element and J is covalently bridged to L^A , or with two R' groups when J is a group 15 element and J is not covalently bridged to L^A , or is unsubstituted when J is a Group 16 element and J is covalently bridged to L^A , and each substituent group R' is, independently, a radical selected from: hydrocarbyl, hydrocarbylsilyl or hydrocarbylgermyl radicals having 1 to 30 carbon, silicon or germanium atoms; substituted hydrocarbyl, silyl-hydrocarbyl or germyl-hydrocarbyl radicals as defined wherein one or more hydrogen atoms is replaced by a C_{1-20} hydrocarbyl radical, halogen radical, an amido radical, a phosphido radical, an alkoxy radical, or an aryloxy radical; halogen radicals; amido radicals; phosphido radicals; alkoxy radicals; or alkylborido radicals. A preferred J group when unbridged to L^A is one where each R' is independently a bulky substituent such as tert-butyl or trimethyl silyl, see copending application U.S. application serial number 08/833,146, filed April 4, 1997, and filed internationally as PCT/US96/17224, incorporated by reference for purposes of U.S. patent practice.

The term "asymmetric" as applied for two L^A and L^B rings means, for the purposes of this description and the claims derived therefrom, the number or type of ring substituents on the L^A and L^B rings is different. Thus for certain embodiments of the invention metallocene catalyst compound containing two π -bonded rings and a total number of substituents on the rings equal to 3, two generally defined substituents can be on L^A and the primary carbon-containing substituent of the invention then is on the L^B ring. For certain embodiments of the invention metallocene catalyst compound containing two π -bonded

cyclopentadienyl)(n-propyl-cyclopentadienyl) zirconium dichloride or dimethyl, (pentamethyl-cyclopentadienyl)(n-propyl-cyclopentadienyl) zirconium dichloride or dimethyl, (tetramethyl-cyclopentadienyl)dimethylsilyl(3-n-propyl-cyclopentadienyl)

cyclopentadienyl)dimethylsilyl(2-methyl-4-n-propylcyclopentadienyl) zirconium dichloride or dimethyl, (indenyl)isopropylidene(3-n-propyl-cyclopentadienyl) zirconium dichloride or dimethyl, (indenyl)dimethylsilyl(3-n-propyl-cyclopentadienyl) hafnium dichloride or

zirconium dichloride or dimethyl, (1-methyl-3-ethylcyclopentadienyl)(1-methyl-3-n-propylcyclopentadienyl) zirconocene, (1,2,4-trimethyl-3,5-di-n-butylcyclopentadienyl) zirconium dichloride or dimethyl, (1-n-butylindeyl)(4-phenylindenyl) zirconium dichloride

substituent bonded to one ring through a primary carbon atom. Where fused rings are part of the ring substitution pattern each such fused ring is counted as two substituents on its respective cyclopentadienyl ring. Thus indenyl ligands are considered to be

The catalyst compounds described above are suitable for olefin polymerization in

monocyclopentadienyl and biscyclopentadienyl catalysts will be instructive. See, for example, U.S. patents 5,198,401, 5,324,800, 5,502,124, 5,635,573, 5,536,796 and

International publications WO 92/00333 and WO 96/33227. Generally speaking, the polymerization process comprises contacting one or more olefinically unsaturated monomers with an activated catalyst compound of the invention, activation occurring by reaction or interaction with a cocatalyst activator compound suitable for activation of known metallocene compounds into active, insertion polymerization catalyst compounds. The teachings as to olefin polymerization in the references above are incorporated by reference for purposes of U.S. patent practice. As is well-known in the art, suitable polymerizable olefins include α -olefins containing 2 or more carbon atoms, preferably C₂ to C₈ α -olefins, cyclic olefins, preferably norbornene or alkyl-substituted norbornenes, non-conjugated diolefins, and vinyl aromatic monomers, preferably styrene and alkyl-substituted styrene monomers. Additionally, when the invention metallocene contains only one π -bonded ring bridged to a Group 15 or 16 heteroatom, geminally disubstituted olefins, such as isobutylene, will be polymerizable in accordance with the teachings of U.S. application serial number 08/651,030, filed on May 21, 1996, incorporated by reference for purposes of U.S. patent practice.

The catalysts according to the invention are particularly suited to use in known gas phase or slurry copolymerization processes where heterogeneous catalysts are typically used. The heterogeneous catalysts of the invention are typically supported on inert support particles, which may be formed from inorganic refractory oxide or polymeric materials, which are then used in a gas phase or liquid process wherein the monomers are contacted with the supported catalysts. The teachings and descriptions of the background art are incorporated by reference for purposes of U.S. patent practice and are specific to process conditions and reagents useful with the catalyst system of this invention.

For olefin polymerization, the metallocene compounds of the invention may be activated by use of the traditional activation cocatalysts, specifically including the use of alkyl aluminum compounds, alkyl alumoxane compounds and any ionizing activators, such as those represented by aryl-substituted boron compounds, e.g., nitrogen-containing salts, carbenium or phosphonium salts, metal salts and neutral Lewis acid compounds. Each activation method is well-documented in the field of metallocene art. Related means of activation, such as the use of alkyl aluminum alkylation agents used to convert metallocene

halide compounds to hydride or alkyl group-containing compounds prior to activation with the ionic activator compounds will be suitable in accordance with the inventions. Additionally, the use of supported activators, where such are stable compounds, will be suitable in accordance with the invention for both activation and support. See, for example, 5 U.S. patents 5,427,991 and 5,643,847, each of which is incorporated by reference for purposes of U.S. patent practice.

The use of organometallic compounds as scavenging compounds in the olefin polymerization processes of the invention will also be suitable. Alkyl aluminum compounds 10 such as triethyl aluminum, triisobutyl aluminum, tri-n-octyl aluminum, methylalumoxane and isobutylalumoxane are well-known in the art.

Suitable gas phase processes are illustrated U.S. patents 4,543,399, 4,588,790, 5,028,670, 5,352,749, 5,382,638, 5,405,922, 5,422,999, 5,436,304, 5,453,471, and 15 5,463,999, and International applications WO 94/28032, WO 95/07942 and WO 96/00245. Each is incorporated by reference for purposes of U.S. patent practice. Typically the processes are conducted at temperatures of from about -100 °C to 150 °C, preferably from about 40 °C to 120°C, at pressures up to about 7000 kPa, typically from about 690 kPa to 2415 kPa. Continuous processes using fluidized beds and recycle streams as the fluidizing 20 medium are preferred.

Slurry polymerization processes in which the immobilized catalyst systems of this invention may be used are typically described as those in which the polymerization medium can be either a liquid monomer, like propylene, or a hydrocarbon solvent or diluent, 25 advantageously aliphatic paraffin such as propane, isobutane, hexane, heptane, cyclohexane, etc. or an aromatic one such as toluene. The polymerization temperatures may be those considered low, e.g., less than 50 °C, preferably 0 - 30 °C, or may be in a higher range, such as up to about 150 °C, preferably from 50 °C up to about 80 °C, or at any ranges between the end points indicated. Pressures can vary from about 100 to about 30 700 psia (0.76-4.8 MPa. Additional description is given in U.S. patents 5,274,056 and 4,182,810 and WO 94/21962 which are incorporated by reference for purposes of U.S. patent practice.

The immobilized catalyst systems of the invention may be prepared by any effective method of supporting other coordination catalyst systems, effective meaning that the catalyst so prepared can be used for preparing polymer in a heterogeneous polymerization process. Preferred methods include those referred to in copending U.S. application 08/466,547, filed 6 June 1995, and in its counterpart WO 96/00245. In accordance with this method, as illustrated in the examples below, the transition metal compound is combined with an activator compound in solvent to prepare a precursor solution which is added to a porous support particle in such a manner that the total solvent volume exceeds the total particle pore volume but is less than that at which the formation of a slurry is observed.

The activated catalyst may also be supported in accordance with WO 91/0882 and WO 94/03506, particularly when using ionizing activators providing electronically stabilizing non-coordinating anions. In this method, inorganic oxide particle supports are treated with a Lewis acid to neutralize any hydroxyl groups remaining on the surfaces after thorough drying and prior to the adsorption of the activated catalyst complex from the solution in which it is added.

The support method of Example 11-16 in copending U.S. application Ser. No. 08/549,991, filed 30 October 1995, and in WO 96/08520 will also be suitable in accordance with this invention.

Additional methods appear in the following descriptions for metallocene catalysts, these methods will be suitable as well for the invention catalyst systems. U.S. Patent No. 4,937,217 generally describes a mixture of trimethylaluminum and triethylaluminum added to an undehydrated silica to which a metallocene catalyst component is then added. EP-308177-B1 generally describes adding a wet monomer to a reactor containing a metallocene, trialkylaluminum and undehydrated silica. U.S. Patent Nos. 4,912,075, 4,935,397 and 4,937,301 generally relate to adding trimethylaluminum to an undehydrated silica and then adding a metallocene to form a dry supported catalyst system. U.S. Patent No. 4,914,253 describes adding trimethylaluminum to undehydrated silica, adding a metallocene and then drying the resulting supported catalyst system with an amount of

hydrogen to produce a polyethylene wax. U.S. Patent Nos. 5,008,228, 5,086,025 and 5,147,949 generally describe forming a dry supported catalyst system by the addition of trimethylaluminum to a water impregnated silica to form alumoxane in situ and then adding the metallocene. U.S. Patent Nos. 4,808,561, 4,897,455 and 4,701,432 describe techniques to form a supported catalyst where the inert carrier, typically silica, is calcined and contacted with a metallocene(s) and an activator/cocatalyst component. U.S. Patent No. 5,238,892 describes forming a dry supported catalyst system by mixing a metallocene with an alkyl aluminum and then adding undehydrated silica. U.S. Patent No. 5,240,894 generally pertains to forming a supported metallocene/alumoxane catalyst system by forming a metallocene/alumoxane reaction solution, adding a porous carrier, and evaporating the resulting slurry to remove residual solvent from the carrier.

Polymeric carriers will also be suitable in accordance with the invention, see for example the descriptions in WO 95/15815 and U.S. patent 5,427,991. As taught for metallocene catalysts in these documents, the catalyst complexes of this invention may be either adsorbed or absorbed, on the polymeric supports, particularly if made up of porous particles, or may be chemically bound through functional groups covalently bound to or in the polymer chains.

Suitable solid particle supports are typically comprised of polymeric or refractory oxide materials, each being preferably porous. any support material, preferably a porous support material, such as for example, talc, inorganic oxides, inorganic chlorides, for example magnesium chloride and resinous support materials such as polystyrene polyolefin or polymeric compounds or any other organic support material and the like that has an average particle size preferably greater than 10 μm .

The preferred support materials are inorganic oxide materials, which include those from the Periodic Table of Elements of Groups 2, 3, 4, 5, 13 or 14 metal or metalloid oxides. In a preferred embodiment, the catalyst support materials include silica, alumina, silica-alumina, and mixtures thereof. Other inorganic oxides that may be employed either alone or in combination with the silica, alumina or silica-alumina are magnesia, titania, zirconia, and the like.

It is preferred that the carrier of the catalyst of this invention has a surface area in the range of from about 10 to about 700 m²/g, pore volume in the range of from about 0.1 to about 4.0 cc/g and average particle size in the range of from about 10 to about 500 μm.

5 More preferably, the surface area is in the range of from about 50 to about 500 m²/g, pore volume of from about 0.5 to about 3.5 cc/g and average particle size of from about 20 to about 200 μm. Most preferably the surface area range is from about 100 to about 400 m²/g, pore volume from about 0.8 to about 3.0 cc/g and average particle size is from about 30 to about 100 μm. The pore size of the carrier of the invention typically has pore size in
10 the range of from 10 to 1000 Angstroms, preferably 50 to about 500 Angstroms, and most preferably 75 to about 350 Angstroms.

The above documents typically discuss specific methods of supporting metallocene catalysts. Generally the procedures that follow will be suitable. An aluminoxane, such as
15 methylaluminoxane or modified alumoxane, or other suitable cocatalyst activator such as Al(CH₃)₃, Al(CH₂CH₃)₂Cl, B(C₆F₅)₃, [C₆H₅NMe₂H]+[B(C₆F₅)₄]-, [(C₆H₅)₃C]+[B(C₆F₅)₄]-, [H]+[PF₆]-, [Ag]+[BF₄]-, [Ag]+[PF₆]+, or [Ag]+[B(C₆F₅)₄]- is combined with one or more transition metal complexes in an appropriate solvent to form a precursor solution. A suitable support, preferably porous, is charged to a vessel and the precursor solution is
20 added with stirring. The mixture may be mixed by hand with a spatula, by a rotating stirrer with wire loops such as a Kitchen Aid dough mixer, by metal blades rotating at high speed such as in a Wehring blender, by a helical ribbon bladed mixer, by shaking, tumbling, fluidized bed mixing, by paddle or propeller blades on a rotating stir shaft, or other appropriate means. The total amount of solvent used to form the precursor suspension or
25 solution may be less than the pore volume of the support as in impregnation to incipient wetness, or greater than the pore volume of the support such that a slurry is formed, or an amount in between such that a solution-finely divided support mixture is neither free flowing nor a slurry. Solution may be added to support or vice versa as appropriate to the mixing method. If desired the liquids may be removed by purging with an inert gas or
30 under vacuum.

The products of the polymerization processes described above, using the invention catalyst compounds, are typically those having narrow composition distribution (CDBI ≥

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60) with melt index ratios less than about 35, preferably 30 and more preferably less than about 25. The MWD (M_w/M_n) can range from about 2-15, preferably 2-10, and even 2.5-5. Where greater than about 4.5, melt processing of the copolymer products are improved, where less than 4.5 both of less clarity and less uniformity of end products are improved.

- 5 The molecular weight, as expressed in terms of its polyethylene melt index (MI; 2.16 kg/cm², 190 °C, ASTM D 1238) will typically range from 0.2 to 10 as determined by specific catalyst choice and selection of known operating polymerization conditions such as hydrogen addition and polymerization temperature. It has been additionally observed that ethylene copolymers having high melt strength (MS; $\geq 6.0 - 6.0 \times \log(\text{MI})$, preferably \geq
- 10 $8.0 - 6.0 \times \log(\text{MI})$) are made possible with certain catalysts of the invention, this being particularly surprising in that high melt index ratios (MIR; I_{21}/I_2) values (e.g., ≥ 35) previously had been thought to be a necessary parameter for achieving high values of melt strength. As illustrated in example 14 below, bridged, biscyclopentadienyl catalyst compounds according to the invention can yield a surprising combination of low MIR and
- 15 high melt strength. This combination results in improved bubble strength for blown film and reduced problems with "neck in" for cast or extruded film without the expected significant reduction of film toughness typically observed with ethylene polymers having high MIR and high MS.

- 20 The polymer characterizations presented in this application were conducted under the following conditions and procedures. MI was determined as described above. MIR is described as the ratio of the I_{21} to I_2 in accordance with ASTM D-1238. All of M_w , M_n , and M_w/M_n (MWD) were determined by gel permeation chromatography (GPC) using a DRI differential refraction index detector, i.e., a Waters 150C GPC instrument with DRI
- 25 detectors. CDBI was determined in accordance with the method described in columns 7 and 8 of WO 93/03093. Melt strength was determined using a Gottfert Rheotens Melt Strength apparatus measuring at 190 °C in conjunction with an Instron Capillary Rheometer. The capillary die was set at 0.6 in. diameter x 1 in. length and the extrudate rate was set at the die exit at 3 in./ min. The take off gears of the apparatus were set at 100
- 30 mm from the die exit. The take-up speed for the extrudate was progressively increased in accordance with the program of an Acceleration Programmer Model 459117 at a setting of 12. Density was measured in accordance with ASTM d-1505. The Average Particle Size

(APS) was measured by determining the weight of material collected on a series of U.S. Standard sieves and determining the weight average particle size in micrometers based on the sieve series used.

5

EXAMPLES

I. Unbridged Biscyclopentadienyl Catalyst Systems

10 **Example 1 (Invention)** - *(n-propylcyclopentadienyl) (pentamethylcyclopentadienyl) zirconium dichloride*

Metallocene Synthesis.

15 Pentamethylcyclopentadienyl zirconium trichloride (25 g, 75 mmol) was dissolved in 200 cm³ of a 50:50 mixture of toluene and tetrahydrofuran. The reaction flask was equipped with a mechanical stirrer and cooled to -78°C. 75 cm³ of 1.0 M solution of sodium-*n*-propylcyclopentadienide (corresponding to 75 mmol *n*-propylcyclopentadiene) in toluene/tetrahydrofuran was then added slowly using a pressure-equilibrated addition
20 funnel. The reaction was allowed to continue over 16 hours while the temperature warmed to 22°C. The solvent was then removed under reduced pressure at 45°C. The resulting crude product was extracted repeatedly with hexane. The hexane extracts were concentrated and the pure title compound was precipitated out at -34°C. The purity of the compound was confirmed with ¹H-NMR (500 MHz).

25

Preparation of Supported Catalyst.

a) Methylalumoxane (1091 cm³ of 30 wt-% solution in toluene) was charged into a 2-gallon reaction vessel. 1576 cm³ of fresh toluene was added. Then a 10 wt-%
30 solution of 14.8 g of *(n*-propylcyclopentadienyl)(pentamethylcyclopentadienyl) zirconium dichloride in toluene was added. The temperature was maintained at 27°C and the mixture stirred for 1 hour.

b) 800 g of a Davison 948 sample dehydrated at 600°C was charged into a 2-gallon reaction vessel at 27°C. The solution of methylalumoxane and metallocene from above was added onto the silica in two equal portions. Then an additional 450 cm³ toluene
35 was added to the slurry. After 20 minutes, a solution of 5.7 g of N,N-bis(2-hydroxyethyl) octadecylamine in 50 cm³ toluene was added and stirring

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continued for another 30 minutes. The final catalyst was then dried to free-flowing powder at 80°C under vacuum.

Polymerization.

5

The supported catalyst described above was then tested in a pilot plant. The catalyst was fed continuously into a fluid bed gas-phase pilot plant reactor (internal diameter of 16¼ inches) maintained at 85°C and 300 psig total reactor pressure. The product was withdrawn continuously through a product discharge outlet to maintain a constant bed height in the reactor. The composition of the gas phase, and operating conditions for the reactor, are summarized in Table I below.

10

Example 2 *(n-propylcyclopentadienyl)-(pentamethylcyclopentadienyl) zirconium dichloride)*

15

550 g of a Davison 948 sample dehydrated at 200°C was charged into a 2-gallon reaction vessel at 27°C. 1280 cm³ of a 30 wt-% methylalumoxane solution in toluene was added followed by 1500 cm³ fresh toluene. The temperature was then raised to 68°C and stirring continued for 4 hours. 26.7 g of (n-propylcyclopentadienyl)-(pentamethylcyclopentadienyl) zirconium dichloride in 100 cm³ toluene was then added and stirring continued for an additional 2 hours. The final catalyst was dried to free-flowing powder under vacuum at 68°C.

20

25

The supported catalyst was used in the polymerization of ethylene with 1-hexene in a gas-phase pilot unit as described in example 1 except that triethylaluminum was used as scavenger during the polymerization. The results are shown in Table I below.

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Comparative Example 3 (*bis(n-propylcyclopentadienyl) zirconium dichloride*)

Preparation of Supported Catalyst.

- 5 a) Methylalumoxane (1070 cm³ of 30 wt-% solution in toluene) was charged into a 2-gallon reaction vessel. 1611 cm³ of fresh toluene was added. Then a 10 wt-% solution of 13.5 g of *bis(n-propylcyclopentadienyl) zirconium dichloride* in toluene was added. The temperature was maintained at 27°C and the mixture stirred for 1 hour.
- 10 b) 800 g of a Davison 948 sample dehydrated at 600°C was charged into a 2-gallon reaction vessel at 27°C. The solution of methylalumoxane and metallocene from above was added onto the silica in two equal portions. Then an additional 450 cm³ toluene was added to the slurry. After 20 minutes, a solution of 5.7 g of N,N-bis(2-hydroxyethyl) octadecylamine in 50 cm³ toluene was added and stirring continued for another 30 minutes. The final catalyst was then dried to free-flowing powder at 80°C under vacuum.

Polymerization.

The supported catalyst was used in the polymerization of ethylene with 1-hexene in a gas-phase pilot unit as described in example 1. The results are shown in Table I below. Though illustrating low MIR polymer products, the comparison of Figures 1 and 2 illustrate that the polymer of Ex. 3 has a dual melting point peak instead of the single melting point peak of the polymers from the invention catalysts. The second melt DSC traces of Figures 1 and 2 were obtained on a Perkin-Elmer instrument using ASTM D3417-83 standard procedures.

Table I

Example	1	2	3(C)
Ethylene (mol-%)	50	50	49.6
1-Hexene (mol-%)	1.97	0.89	1.20
Hydrogen (ppm)	100	126	279
Nitrogen	balance	balance	balance
Catalyst Productivity (g/g)	4302	3720	9193
Melt Index (I ₂)	1.02	2.33	2.81
Melt Index Ratio (MIR)(I ₂ /I ₂₁)	15	20.9	18
Resin Density	0.9162	0.9220	0.9124
Polymer APS (μm)	910	579	1181

Example 4 (Invention) - *(n-propylcyclopentadienyl)(pentamethylcyclopentadienyl) zirconium dichloride*

5 Preparation of Supported Catalyst:

a) Methylalumoxane (1361 cm³ of 30 wt-% solution in toluene) was charged into a 2-gallon reaction vessel. 1970 cm³ of fresh toluene was added. Then a solution of 18.5 g of *(n-propylcyclopentadienyl) (pentamethylcyclopentadienyl) zirconium dichloride* in 335 cm³ toluene was added. The temperature was maintained at 27°C and the mixture stirred for 1 hour.

b) 1000 g of a Davison 948 sample dehydrated at 600°C was charged into a 2-gallon reaction vessel at 27°C. The solution of methylalumoxane and metallocene from above was added onto the silica in two equal portions. Then an additional 250 cm³ toluene was added to the slurry. After 20 minutes, a solution of 6.8 g of N,N-bis(2-hydroxyethyl) octadecylamine in 70 cm³ toluene was added and stirring continued for another 20 minutes. The final catalyst was then dried to free-flowing powder at 68°C under vacuum.

20 Polymerization:

The catalyst was then tested for ethylene/1-hexene co-polymerization in a continuous fluid bed gas-phase reactor operated at 300 psig total pressure, 79.4°C reactor temperature, and 1.6 ft/s cycle gas velocity. The catalyst was fed at a rate that maintained a constant rate of product discharge from the reactor. The reactor gas mixture was composed of 35% ethylene, 1.08 % 1-hexene and 90 ppm H₂. Sample was collected after 5 bed-turnovers and analyzed for properties shown in Table II below.

Example 5 (Invention) - *(n-butylcyclopentadienyl)(pentamethylcyclopentadienyl) zirconium dichloride*

Preparation of Supported Catalyst:

5

A solution of methylalumoxane (MAO) and metallocene was formed by adding 55 cm³ of 30 wt-% MAO solution in toluene onto 0.895 g of *(n-butylcyclopentadienyl)(pentamethylcyclopentadienyl) zirconium dichloride* in a vial. 120 cm³ of fresh toluene was added, and the mixture stirred for 45 minutes at 25°C. This pre-mixed solution of the

10 MAO and the metallocene was then added onto 40 g of Davison 948 silica dried to 600°C. The resulting slurry was stirred for 1 hour at 25°C. Then a solution of 0.28 g of N,N-bis(2-hydroxyethyl) octadecylamine in 20 cm³ toluene was added, and stirring continued for another 30 minutes. The final catalyst was then dried to free-flowing powder under vacuum at 65°C

15

Polymerization:

The catalyst was then tested for ethylene/1-hexene co-polymerization in the continuous fluid bed gas-phase reactor of example 4 operated at 300 psig total pressure, 79.4°C reactor

20 temperature, and 1.6 ft/s cycle gas velocity. The catalyst was fed at a rate that maintained a constant rate of product discharge from the reactor. The reactor gas mixture was composed of 35% ethylene, 1.08 % 1-hexene and 84 ppm H₂. Sample was collected after 5 bed-turnovers and analyzed for properties shown in Table II below.

25 **Example 6 (Comparative)-** *(methylcyclopentadienyl)(pentamethylcyclopentadienyl) zirconium dichloride*

Preparation of Supported Catalyst:

30 A solution of methylalumoxane (MAO) and metallocene was formed by adding 27 cm³ of 30 wt-% MAO solution in toluene onto 0.343 g of *(methylcyclopentadienyl)(pentamethylcyclopentadienyl) zirconium dichloride* in a vial. 100 cm³ of fresh toluene was

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added, and the mixture stirred for 45 minutes at 25°C. This pre-mixed solution of the MAO and the metallocene was then added onto 20 g of Davison 948 silica dried to 600°C. The resulting slurry was stirred for 1 hour at 25°C. Then a solution of 0.15 g of N,N-bis(2-hydroxyethyl) octadecylamine in 20 cm³ toluene was added, and stirring
 5 continued for another 30 minutes. The final catalyst was then dried to free-flowing powder under vacuum at 65°C.

Polymerization:

10 The catalyst was then tested for ethylene/1-hexene co-polymerization in the above continuous fluid bed gas-phase reactor operated at 300 psig total pressure, 76.7°C reactor temperature, and 0.66 ft/s cycle gas velocity. The catalyst was fed at a rate that maintained a constant rate of product discharge from the reactor. The reactor gas mixture was composed of 35% ethylene, 1.13 % 1-hexene and 147 ppm H₂. Sample was collected
 15 after 5 bed-turnovers and analyzed for properties shown in Table II below.

Example 7 (Invention) - (*n*-propylcyclopentadienyl) (tetramethylcyclopentadienyl) zirconium dichloride

20 ***Preparation of Supported Catalyst:***

a) Methylalumoxane (1361 cm³ of 30 wt-% solution in toluene) was charged into a 2-gallon reaction vessel. 1970 cm³ of fresh toluene was added. Then a solution of 18.0 g of (*n*-propylcyclopentadienyl) (tetramethylcyclopentadienyl) zirconium dichloride in
 25 335 cm³ toluene was added. The temperature was maintained at 27°C and the mixture stirred for 1 hour.

b) 1000 g of a Davison 948 sample dehydrated at 600°C was charged into a 2-gallon reaction vessel at 27°C. The solution of methylalumoxane and metallocene from above was added onto the silica in two equal portions. Then an additional 250 cm³ toluene
 30 was added to the slurry. After 20 minutes, a solution of 6.8 g of N,N-bis(2-hydroxyethyl) octadecylamine in 70 cm³ toluene was added and stirring

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continued for another 20 minutes. The final catalyst was then dried to free-flowing powder at 68°C under vacuum.

Polymerization:

5

The catalyst was then tested for ethylene/1-hexene co-polymerization in a the above continuous fluid bed gas-phase reactor operated at 300 psig total pressure, 79.4°C reactor temperature, and 1.6 ft/s cycle gas velocity. The catalyst was fed at a rate that maintained a constant rate of product discharge from the reactor. The reactor gas mixture was composed of 35% ethylene, 0.87 % 1-hexene and 103 ppm H₂ . Sample was collected after 5 bed-turnovers and analyzed for properties shown in Table II below.

10

Example 8 (Comparative) - (cyclopentadienyl) (tetramethylcyclopentadienyl) zirconium dichloride

15

Preparation of Supported Catalyst:

20

A solution of methylalumoxane (MAO) and metallocene was formed by adding 27 cm³ of 30 wt-% MAO solution in toluene onto 0.317 g of (cyclopentadienyl) (tetramethylcyclopentadienyl) zirconium dichloride in a vial. 100 cm³ of fresh toluene was added, and the mixture stirred for 45 minutes at 25°C. This pre-mixed solution of the MAO and the metallocene was then added onto 20 g of Davison 948 silica dried to 600°C. The resulting slurry was stirred for 1 hour at 25°C. Then a solution of 0.15 g of N,N-bis(2-hydroxyethyl) octadecylamine in 20 cm³ toluene was added, and stirring continued for another 30 minutes. The final catalyst was then dried to free-flowing powder under vacuum at 65°C.

25

Polymerization :

30

The catalyst was then tested for ethylene/1-hexene co-polymerization in the above continuous fluid bed gas-phase reactor operated at 300 psig total pressure, 71.1°C reactor temperature, and 0.67 ft/s cycle gas velocity. The catalyst was fed at a rate that maintained

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a constant rate of product discharge from the reactor. The reactor gas mixture was composed of 30% ethylene, 0.91 % 1-hexene and 267 ppm H₂ . Sample was collected after 5 bed-turnovers and analyzed for properties shown in Table II below.

5 **Example 9 (Comparative) - (methylcyclopentadienyl) (tetramethylcyclopentadienyl) zirconium dichloride**

Preparation of Supported Catalyst:

- 10 A solution of methylalumoxane (MAO) and metallocene was formed by adding 13.6 cm³ of 30 wt-% MAO solution in toluene onto 0.1932 g of (methylcyclopentadienyl) (tetramethylcyclopentadienyl) zirconium dichloride in a vial. 20 cm³ of fresh toluene was added, and the mixture stirred for 45 minutes at 25°C. This pre-mixed solution of the MAO and the metallocene was then added onto 10 g of Davison 948 silica dried to 600°C.
- 15 The resulting slurry was stirred for 1 hour at 25°C. Then a solution of 0.0699 g of N,N-bis(2-hydroxyethyl) octadecylamine in 20 cm³ toluene was added, and stirring continued for another 30 minutes. The final catalyst was then dried to free-flowing powder under vacuum at 65°C.

20 ***Polymerization:***

- The catalyst was tested for the co-polymerization of ethylene/1-butene in a semi-batch gas-phase reactor at 85°C. The pressure in the reactor was held constant by continuously feeding 5 mol-% 1-butene in ethylene to compensate for any pressure change due to
- 25 polymerization. After 1 h, the polymer formed was separated from the seed bed material and analyzed for resin molecular properties shown in Table II below.

Example 10 (Invention) - (*n*-propylcyclopentadienyl) (pentamethylcyclopentadienyl) zirconium dichloride

Polymerization:

5

The supported catalyst made as in Example 1 above was tested for ethylene/1-hexene copolymerization in a batch slurry reactor using isobutane as diluent. The reactor was operated at 325 psig total pressure, 130 psi ethylene partial pressure, and 85°C reactor temperature. 60 cm³ of 1-hexene was added to depress the density of the polymer. The properties of the formed polymer are shown in Table II below.

10

Example 11 (Invention) - (*n*-propylcyclopentadienyl) (tetramethylcyclopentadienyl) zirconium dichloride

15

Polymerization:

The supported catalyst made as in Example 4 above was tested for ethylene/1-hexene copolymerization in a batch slurry reactor using isobutane as diluent. The reactor was operated at 325 psig total pressure, 130 psi ethylene partial pressure, and 85°C reactor temperature. 60 cm³ of 1-hexene was added to depress the density of the polymer. The properties of the formed polymer are shown in Table II below.

20

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Table II

Example	Density (g/cc)	MI (I ₂)	MIR (I ₂₁ /I ₂)	Productivity (g/g-hr)
4	0.9196	1.49	17.5	2213
5	0.9181	1.11	18.9	1511
6 (comparative)	0.9184	0.84	31.7	1558
7	0.9170	1.03	18.8	3196
8 (comparative)	0.9179	1.21	46.0	1871
9 (comparative)	0.9223	0.43	35.8	920 (see Note 1)
10	0.9234	0.22	18.3	2458 (see Note 1)
11	0.9194	0.18	18.0	6490 (see Note 1)

Note 1 -- Catalyst productivity expressed as g_{PE} / (g_{CAT} • h • 150 psi)

5 II. Bridged Biscyclopentadienyl Catalyst Systems

Preparation of Supported Catalyst A (*fluorenyl (dimethylsilyl) 3-propylcyclopentadienyl zirconium dichloride*)

10 Fluorenyl (dimethylsilyl) 3-propylcyclopentadienyl zirconium dichloride, 0.092 g, was stirred with 4.0 g 30% MAO (by weight in toluene, Albemarle) and 4.0 g toluene. After complete dissolution, it was mixed with 3.0 g SiO₂ (dried at 600°C, Davison) and dried under high vacuum at room temperature for 12 hours.

15 **Example 12 (Invention) - (*fluorenyl (dimethylsilyl) 3-n-propylcyclopentadienyl zirconium dichloride*)**

Polymerization:

20 Slurry polymerizations were carried out in a 1 L. stainless steel autoclave using 800 ml isobutane as reaction solvent. Cocatalyst used was 1.6 mmol AlEt₃. Ethylene pressure was

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120 psi and 60 ml hexene were used. 50 mg of catalyst A was added to the reaction mixture at a temperature of 150°F. In some instances it was necessary to add 10 mmol H₂ in order to obtain the desired polymer MI. The reaction was run for 40 minutes, then cooled and isobutane removed to obtain the polymer as a granular solid.

5

Table III

<u>Example</u>	<u>H₂</u> (mmol)	<u>Yield</u> (g)	<u>Productivity</u> (g/g-hr)	<u>Density</u> (g/cc)	<u>MI</u>	<u>MIR</u>
12a	10	94	2823	0.9081	0.68	27.8
12b	0	152	4565	0.902	0.2	26
12c	0	162	4865	0.904	0.2	31

Example 13 (Invention) - (*fluorenyl (dimethylsilyl) 2-methyl-3-benzylindenyl zirconium dichloride*)

10

A slurry polymerization similar to the above was performed with a different catalyst according to the invention. It was supported as described above. The resulting MI was 9.58, the density was 0.9154 and the MIR was 21.6.

15

Copolymerization of Ethylene/Hexene in Gas Phase.

Example 14 (Invention) - (*fluorenyl (dimethylsilyl) 3-n-propylcyclopentadienyl zirconium dichloride*)

20

Polymerizations were carried out in the above continuous gas phase unit with regular injections of the catalyst of example 12 under the following conditions: 326 mol ppm H₂, 0.32 mol% hexene, 31.0 mol% ethylene, and a temperature of 169°F. Product characteristics are presented in Table IV.

25

Example 15 (Comparative) *(fluorenyl (dimethylsilyl) 3-methylcyclopentadienyl zirconium dichloride)*

5 Polymerizations were carried out in the above continuous gas phase unit with regular injections of the comparative catalyst under the following conditions: 169.3 mol ppm H₂, 0.35 mol% hexene, 39.9 mol% ethylene at a temperature of 169°F. Product characteristics are presented in Table IV.

Table IV

<u>Example</u>	<u>Productivity</u> (g/g-hr)	<u>Density</u> (g/cc)	<u>MI</u>	<u>MIR</u>	<u>CDBI</u>	<u>MS</u> (cN)
14	1529	0.9184	1.74	21.5	67.3	25.5
15(C)	735	0.9138	1.08	75.2	72.5	5.1

10 We Claim:

CLAIMS

1. An olefin polymerization process comprising contacting ethylene alone or with one or more olefinically unsaturated comonomers under suitable polymerization conditions with a Group 3-6 metallocene catalyst compound comprising a π -bonded ring having one or more C₃ or greater hydrocarbyl, hydrocarbylsilyl or hydrocarbylgermyl substituent said substituent bonded to the ring through a primary carbon atom; and, where the compound contains two π -bonded rings, the total number of substituents on the rings is equal to a number from 3 to 10, said rings being asymmetrically substituted where the number of substituents is 3 or 4.

2. The process of claim 1 wherein said catalyst compound comprises a π -bonded ring having one of said C₃ or greater hydrocarbyl, hydrocarbylsilyl or hydrocarbylgermyl substituents.

3. The process of claim 2 wherein said metallocene compound contains two π -bonded rings not covalently bridged to each other and said rings have four or five methyl groups on the first ring and a C₃ or greater hydrocarbyl, hydrocarbylsilyl or hydrocarbylgermyl substituent on the second ring.

4. The process of claim 1 wherein said metallocene compound contains two π -bonded rings covalently bridged to each other and said C₃ or greater hydrocarbyl, hydrocarbylsilyl or hydrocarbylgermyl substituent is attached at the 3 or 4 position on one of the rings, where the ring carbon covalently bound to the bridge is counted as the 1 position.

5. The process of claim 3 wherein the first of the two rings has four methyl groups.

6. The process of claim 5 wherein the second of the two rings C₃ or greater substituent.

7. A process according to claim 1 wherein the contacting is done under gas phase conditions.

8. A process according to claim 1 wherein the contacting is done under slurry conditions.

5 9. An ethylene homopolymer or copolymer having an $MIR \leq 35$, a $MWD = 2-15$, a $CDBI \geq 60$, and a melt strength $\geq 6.0 - 6.0 \times \log(MI)$.

10. The homopolymer or copolymer of claim 9 wherein the melt strength is $\geq 8.0 - 6.0 \times \log(MI)$.

10

11. The polymer of claim 9 where the MI is 0.3 to 1.2.

12. The polymer of claim 9 where the MIR is \leq than 25.

15 13. The polymer of claim 9 consisting of ethylene.

14. The polymer of claim 9 comprising ethylene and one or more C_3-C_8 α -olefin.

15. The polymer of claim 11 consisting of ethylene.

20

16. The polymer of claim 11 comprising ethylene and one or more C_3-C_8 α -olefin.

17. The polymer of claim 12 consisting of ethylene.

25 18. The polymer of claim 12 comprising ethylene and one or more C_3-C_8 α -olefin.

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ABSTRACT**Olefin Polymerization Process****5****With Alkyl-substituted Metallocenes****10****15**

The invention comprises an olefin polymerization process comprising contacting ethylene alone or with one or more olefinically unsaturated comonomers with a Group 3-6 metallocene catalyst compound comprising one π -bonded ring having a C₃ or greater hydrocarbyl, hydrocarbylsilyl or hydrocarbylgermyl substituent said substituent bonded to the ring through a primary carbon atom; and, where the compound contains two π -bonded rings, the total number of substituents on the rings is equal to a number from 3 to 10, said rings being asymmetrically substituted where the number of substituents is 3 or 4. The invention process is particularly suitable for preparing ethylene copolymers having an MIR less than about 35, while retaining narrow CD even at high comonomer incorporation rates, and with certain embodiments providing ethylene copolymers having improved melt strength with the low MIR.

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Typical DSC Trace for Invention Catalyst
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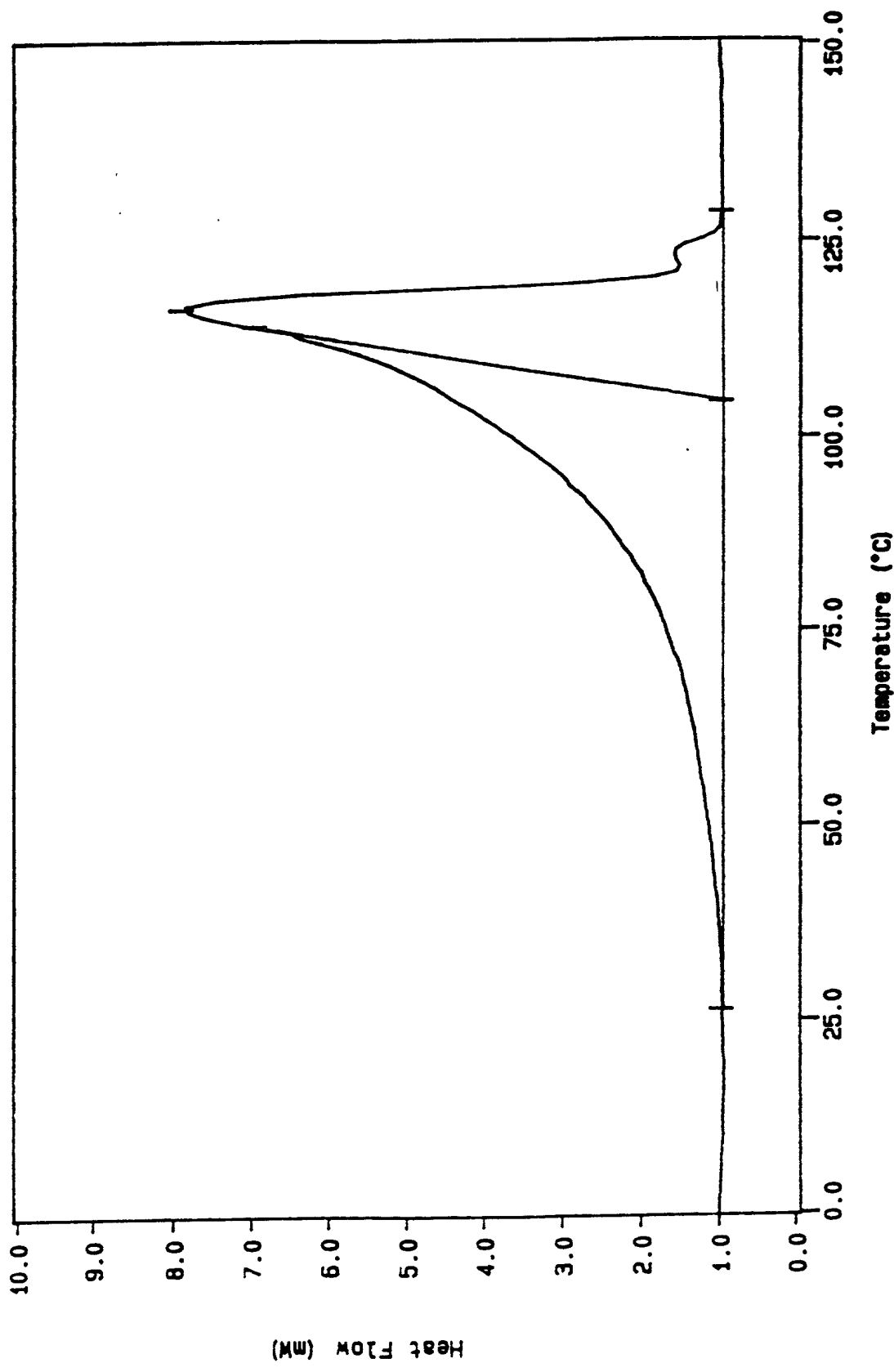


FIG 1

Typical DSC Trace for Comparative Example

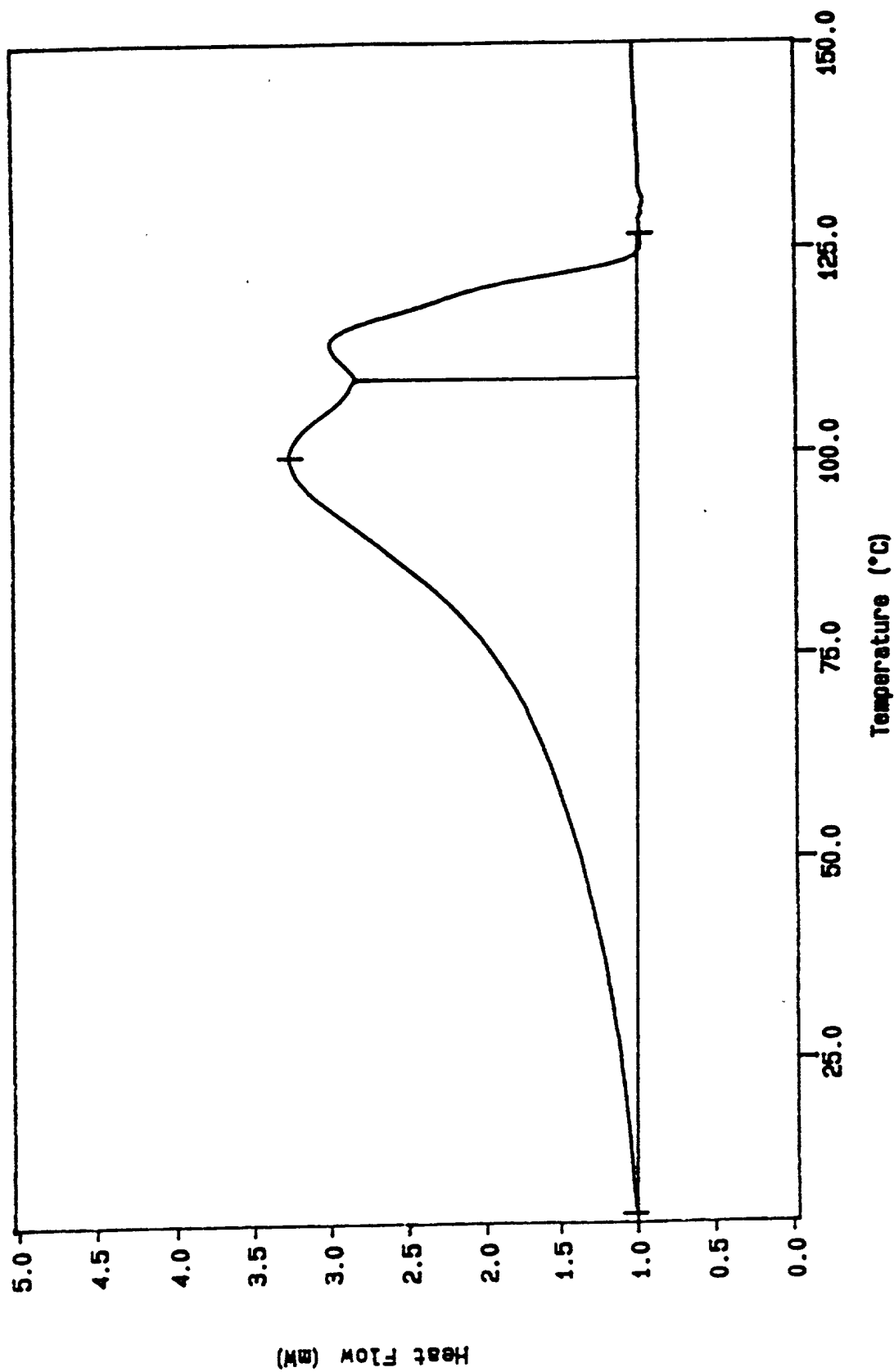


FIG 2

"PATENT"

DECLARATION FOR PATENT APPLICATION

As a below named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name.

I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

OLEFIN POLYMERIZATION PROCESS WITH ALKYL-SUBSTITUTED METALLOCENES

the specification of which is attached hereto unless the following box is checked:

[X] was filed on 07/16/97 Application Serial No. 08/899,902
and was amended on (if applicable).

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above.

I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, § 1.56.

I hereby claim foreign priority benefits under 35 U.S.C. § 119(a)-(d) or § 365(b) of any foreign application(s) for patent or inventor's certificate(s), or § 365(a) of any PCT International application which designated at least one country other than the United States, listed below and have also identified below, by checking the box, any foreign application(s) for patent or inventor's certificate(s), or PCT International application having a filing date before that of the application on which priority is claimed.

Prior Foreign Application(s) Priority Claimed

(Number)

(Country)

(Day/Month/Year Filed)

[]
Yes

[]
No

I hereby claim the benefit under 35 U.S.C. § 119(e)(1)-(2) of any United States provisional application(s) listed below.

60/021,841
(Application Number)

07/16/96
(Filing Date)

I hereby claim the benefit under 35 U.S.C. § 120 of any United States application(s), or § 365(c) of any PCT International application designating the United States, listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in the prior United States or PCT International application in the manner provided by the first paragraph of 35 U.S.C. § 112, I acknowledge the duty to disclose material information which is material to patentability as defined in 37 CFR § 1.56 which became available between the filing date of the prior application and the national or PCT International filing date of this application.

(Application Serial No.)

(Filing Date)

(Status - patented, pending, abandoned)

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) and/or agent(s) to prosecute this application and transact all business in the Patent and Trademark Office connected therewith.

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I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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